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FRACTIONAL EXTRACTION PROCEDURES FOR ENVIRONMENTALLY SIGNIFICANT INORGANIC IONS IN SEDIMENTS, SOILS AND MINE TAILINGS

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FRACTIONAL EXTRACTION PROCEDURES FOR ENVIRONMENTALLY SIGNIFICANT INORGANIC IONS IN SEDIMENTS, SOILS AND MINE TAILINGS

By:

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ABSTRACT

Fractional Extraction Procedures for Environmentally Significant Inorganic Ions in Sediments, Soils and Mine Tailings

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Recent literature on the roles of organic matter, clay, Eh, pH and inter-element effects on "extractable" or "available" fractions of metals associated with soils, sewage sludges and sediments is reviewed in relation to current thinking on laboratory digestion and extraction or leach procedures. Some of the findings can be extended to the study of the leachable or toxic fraction of mine tailings.

Preliminary results on comparisons of extractable metals in sediments by HCl/HNO_3 digestion, hot dilute HCl digestion and cold dilute HCl extraction are discussed in relation to their environmental significance. The study is being continued.

FRACTIONAL EXTRACTION PROCEDURES FOR ENVIRONMENTALLY SIGNIFICANT INORGANIC IONS IN SEDIMENTS, SOILS AND MINE TAILINGS

There is an increasing interest in environmental chemistry in the concept of "extractable" or "available" inorganic ions in sediments, soils and industrial wastes. Processes such as uptake by biota and mobility of pollutants are affected.

Total chemical analysis is useful in establishing long term pollutant potentials and the need or otherwise for further study. If high concentrations are indicated total analysis should be followed up by extraction tests. Unfortunately, total multi-element analysis is tedious and time consuming except in those laboratories equipped with facilities such as powder spectrograph, neutron activation or X-ray fluorescence. Most laboratories have, therefore, opted for partial dissolution procedures with various acid mixtures. (Bennett, 1977; Sulcek et al 1977)

Versions of aqua regia digestion (HCl, HNO_3) are used by a number of environmental laboratories, including the Ontario Ministry of Environment Sediment and Soils Laboratory (Darcel, 1975b) and have been proposed for adoption by the ASTM (Bennett 1974). It has been suggested that the fraction released by this treatment (metals in the interstitial water, adsorption sites, precipitated oxides, hydroxides, phosphates and sulphides and most of the organic matter) is capable of migrating in the upper part of a sediment (Mothersill, 1977) and is often of pollutant origin. Other procedures have been proposed, such as hot dilute hydrochloric acid with some nitric acid (McKown, 1976) and nitric acid-hydrogen peroxide (Krishnamurty & Reddy, 1975).

There is a need for tests designed to assess immediate environmental impact. A wide range of mild extractant procedures have been used ranging from cold water through organic reagents to dilute mineral acids and alkalis. The subject was reviewed by the writer (Darcel, 1975a & b), Jenne and Luoma (1975) and Forstner (1976). "Shake" tests have been most commonly used, partly because of their convenience. Column leach tests, such as those used in the Sediment & Soils Laboratory do, however, more closely simulate environmental conditions, particularly for materials such as industrial wastes. Unlike true total analysis (by wet methods) conditions of the test and chemical composition, degree of crystallinity and physical form (particle size distribution, etc.) of the material govern the quantity of any given parameter released to solution. More recent studies have been directed towards attempting to define factors affecting ion mobility and improved laboratory tests to quantitize "extractable" metals with respect to plant response.

The importance of organic matter is becoming increasingly evident. Organic chelating agents facilitate the transport of metal ions to the root cells of terrestial plants (Halvorsen & Lindsay 1977). Organic matter can also immobilize metals as humic complexes which are then released only on slow decay (Zunino & Martin, 1977). Some organic compounds have been shown to have selective complexing capability, e.g. sewage sludge-soil fulvic acid can complex Cu, Fe and Zn but not Cd or Ni (Sposito et al, 1976).

The role of clay in ion exchange and metal transport is well known. In a study of reservoir sedimentation Pita and Hyne (1975) found that zinc, cadmium and lead were concentrated in the deepest part of the reservoir with a strong correlation between Zn and Pb concentration and water depth, organic content and clay-size fraction. Isolation and analysis of the $< 2\,\mu m$ fraction has proven a useful tool in determining anthropogenic inputs of metals, such as Cr, Cu, Zn, Hg and As (Helmke et al, 1977). Unusually high enrichment of these metals, such as at the surface in sediment cores and at the outfall of a sewage treatment plant was a better indicator than the analysis of the entire samples, with or without quartz correction, because of the lower variability in metal concentration of clay in "unpolluted" controls.

Inter-element effects are also important in ion mobility. As an example, chloride from road salt accumulation can have a significant effect on the solubility of Hg, Zn, Cd and Pb (Hahne & Kroontje, 1973).

pH and Eh are also important with respect to mobility.

High pH results in precipitation reactions for several metals. Leaching of arsenic as the more toxic arsenite can occur at low Eh-pH values (Hess & Blanchchar, 1976). In non-calcareous soils lead solubility was found to be regulated by hydroxy and phosphate formation, dependant on pH (Santillan-Medrano & Jurinak, 1975).

EXTRACTABLE METALS IN SOIL & SLUDGE

EDTA has been widely used as an extractant for soil and sewage sludge. DTPA .005N (diethylenetriaminepentaacetic acid) is proving promising with correlations established between extractable metals, most commonly Fe, Zn, Cu, and Mn, and plant uptake (Randall et al, 1976, Barrau & Berg, 1977). Rule & Graham (1976) used DTPA to determine "labile" Mn, Fe and Zn and Wallingford et al (1975) for "extractable" Mn, Fe, Zn and Cu in beef feed-lot manured soils. Silviera & Sommers (1977) also used DTPA FOR Cu and Zn in soil-sludge mixtures. Of interest is the relationship found between DTPA extractable Cd and Cr III and organic matter and Cation Exchange Capacity (Street et al, 1977).

Strongest correlations for plant response to a specific metal can sometimes be obtained by a specific extractant such as IN ammonium nitrate for Cd (Symeonides & McRae, 1977). IN nitric acid was superior for lead uptake in lettuce whereas .01 N nitric acid was a better extractant for more sensitive oats (John 1972). Correlations may also be improved by including other factors, such as organic matter content and pH in the prediction equation for manganese uptake by oats (Randall et al, 1976).

Water extraction is still finding application, particularly in toxicity studies, such as with waste water sludge (Stover et al 1976). Saturation extracts can also be used to determine toxic concentrations such as the build-up of B, Cu, Mo, Ni, Co, Pb and Cd in sludge treated soils (Bradford et al, 1971, 1975). Distilled water or water adjusted to pH 3 with sulphuric acid have been used for column leach tests for mine tailings (Fuller et al, 1975). Usually, there was little difference in leachable metals between the two conditions due to the high buffering capacity of the material being leached. In a study on the adsorption and desorption of lead and zinc wastes in soil, Jennett and Linneman(1977) found that these metals, once adsorbed, could not be leached by distilled water although they could be by a strong chelating agent prepared from tree leaves.

Inter-element effects also have to be considered, such as between Pb and Cd for corn (Miller et al, 1977) and a P-Zn interaction on P, Zn, Cu, Mn and Fe uptake (Safaya 1976).

Useful information on chemical form and hence mobility for Pb, Zn, Cd, Ni and Cu in sludge-soil mixtures can be obtained by sequential extraction with KNO_3, KF, $Na_4P_2O_7$, EDTA and HNO_3, to determine fractions in exchange, adsorbed, organic, carbonate and sulphide, respectively (Stover, 1976). Chemical form can also be deduced from correlations, such as Pb and Zn with sulphide S in sewage sludge and Cd with organic S, ester sulphate and 0.1 M LiCl extractable inorganic S (Sommers et al, 1977).

Schwertmann (1973) used oxalate extraction for determining iron coatings and concretions. More recently (Schwertmann & Fanning, 1976) dithionite was used in a study of heavy metal associations with the ferro-manganese minerals.

Some workers have attempted to simulate more natural conditions for studying ion mobility using columns and more natural organic leaching solutions such as extract of tree leaves (Jennett & Linneman 1977), municipal landfill leachate (Griffin et al, 1976) and septic tank leachate (Korte et al, 1976).

EXTRACTABLE METALS IN SEDIMENTS

Agemian and Chau (1976) compared total and partial extraction procedures for metals in sediments. It was found that 0.5 N HCl and .05 N EDTA were both suitable for the extraction of 10 metals from aquatic sediments. The 0.5 N HCl procedure was preferred as it was more powerful than EDTA in removing the more strongly bonded metals. Conditions are standardized by shaking 5g of air-dried < 80 mesh material with 100 ml of extractant. The fraction of metal released is considered to be "non-residual".

Sequential extraction procedures have been used in attempts to determine chemical form, such as that used by Gibbs (1973). Magnesium chloride, dithionite-citrate and hypochlorite extractions were used to distinguish metals associated with exchange mechanisms, ferro-manganese coatings and concretions, and organic matter, respectively. Density gradient-zonal centrifugation and particle size distribution have also been used to measure heavy metal associations with carbonate bands, quartz (iron oxide coatings) and illite in the fine fraction (Perhac, 1974). In the waste water discharge of a Cd-Ni battery plant, Cd was associated with carbonates and Ni with organic matter (Francis et al, 1976).

Metals are often associated with ferro-manganese concretions and coatings, dissolved by dithionite treatment. Perhac (1974) found that 90 per cent of the Mn, 50 per cent of the Fe and 10-15 per cent of Cu and Co in some Tennessee sediments were present in this form.

COMPARISON OF EXTRACTION PROCEDURES AT OMOE

Because of restrictions of time and resources it has been possible to conduct only very limited comparisons between the HCl/HNO_3 digestion method used routinely and proposed alternative procedures. Comparison with the 0.5 N HCl cold extraction procedure of Agemian & Chau for non-residual metals in sediments was of interest because of its possible application for the near-shore sediments of the Great Lakes to compare with analyses of deep water sediments by the Canada Centre for Inland Waters. The method also holds promise of distinguishing polluted from background levels.

The hot dilute HCl procedure of McKown was also compared with HCl/HNO_3 digestion. A major advantage of the method, if otherwise satisfactory, is the improved detection limit for metals such as cadmium.

Both procedures have been proposed for adoption by the ASTM.

The three procedures compared in this study are outlined in the Appendix. In all cases the solutions obtained were analysed by routine atomic absorption spectrophotometry. Flame procedures were used except for arsenic (Hydride method).

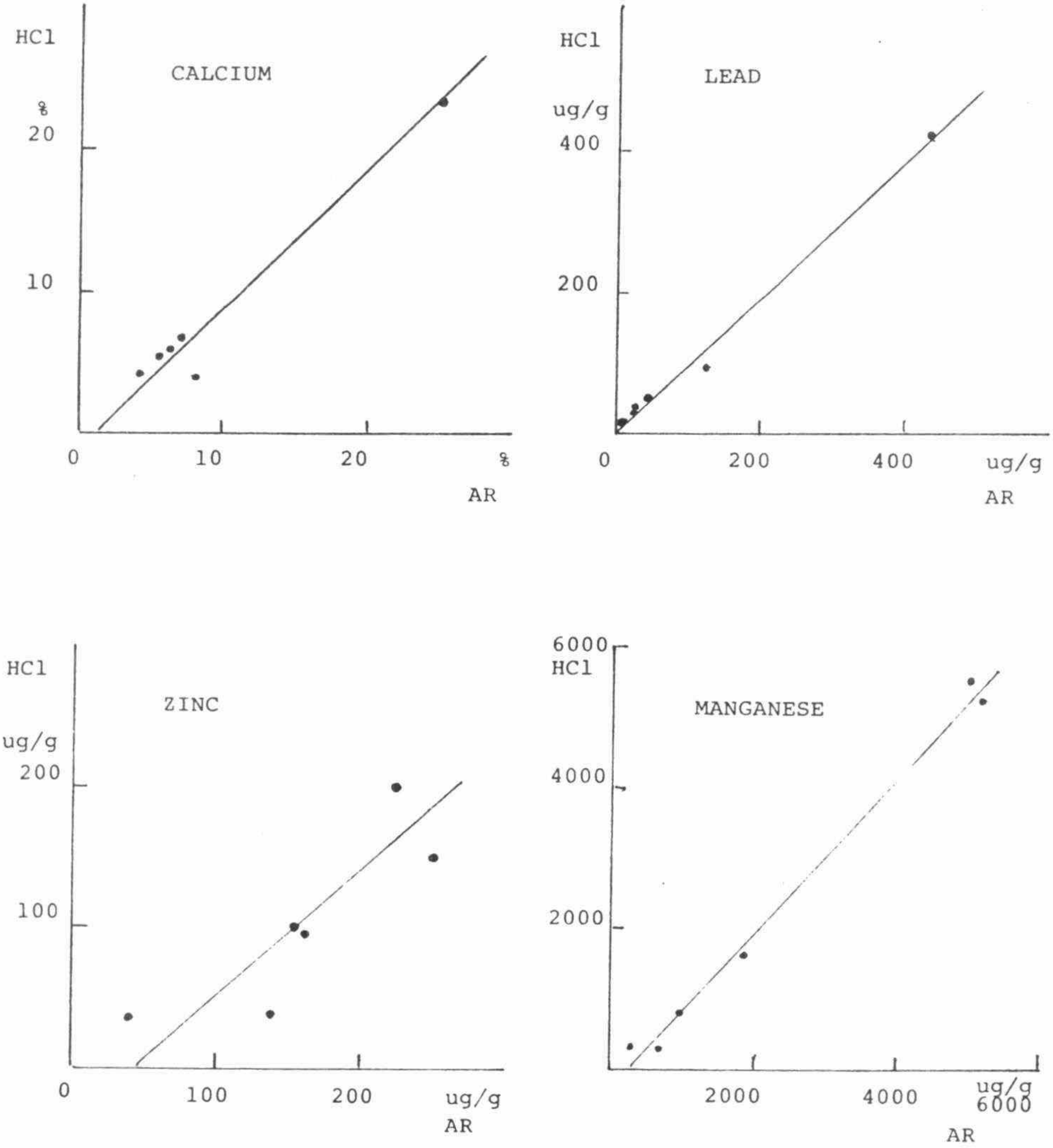
1) 0.5 N HCl COLD EXTRACTION

OMOE data for six samples submitted for an International Joint Commission "round-robin" analyzed by AAS following the OMOE HCl/HNO_3 routine digestion and 0.5 N HCl extraction procedures was used for the comparison.

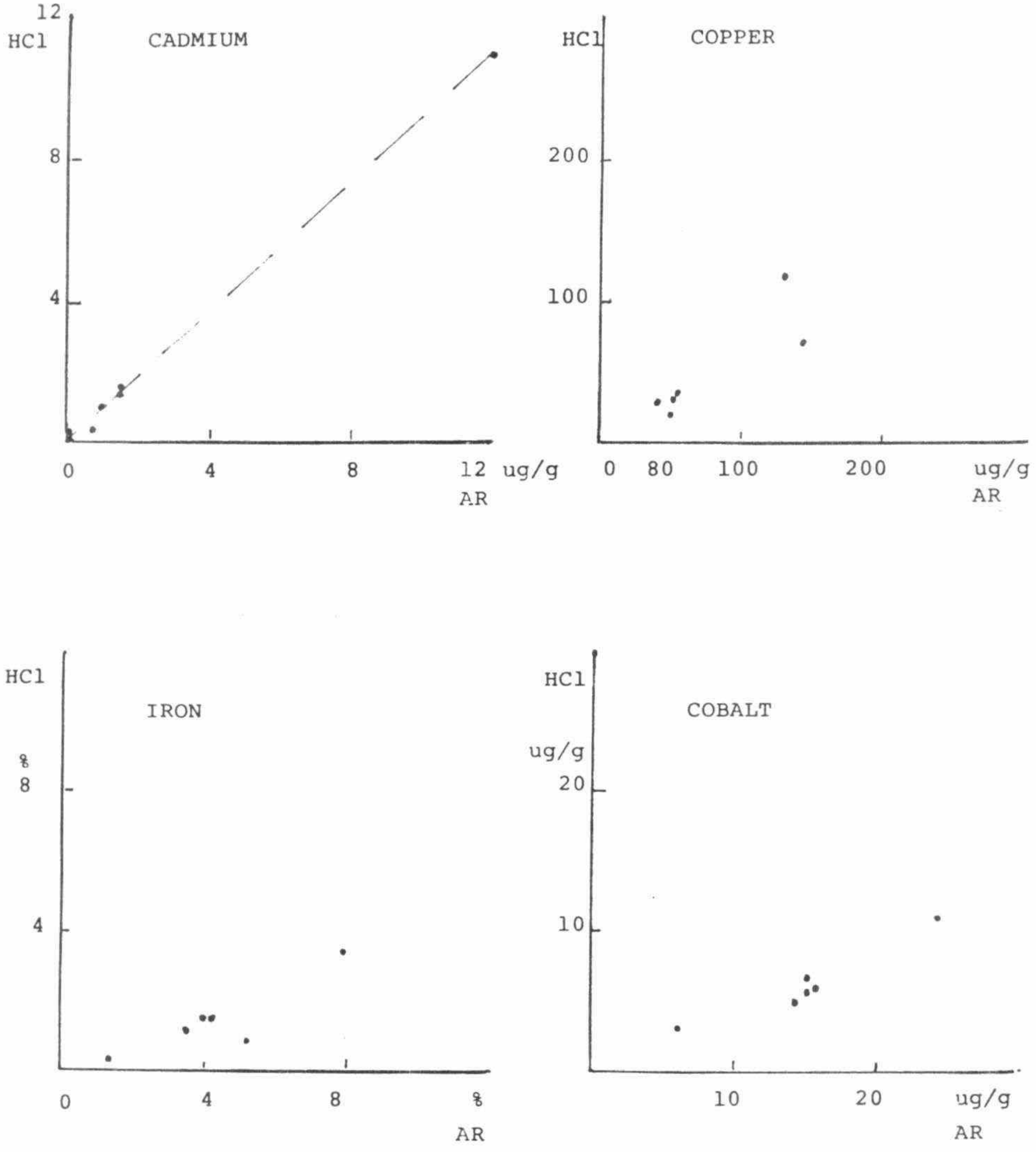
Good correlations were obtained for some metals (Zn, Mn, Ca, Pb and Cd) with higher concentrations measured following HCl/HNO_3 digestion, especially for Zn. No relationship could be seen for Cr, Mg, Al and Ni.

There was some correlation for Cu, Fe and Co. In the case of Fe and Co smaller amounts were extracted by the cold HCl.

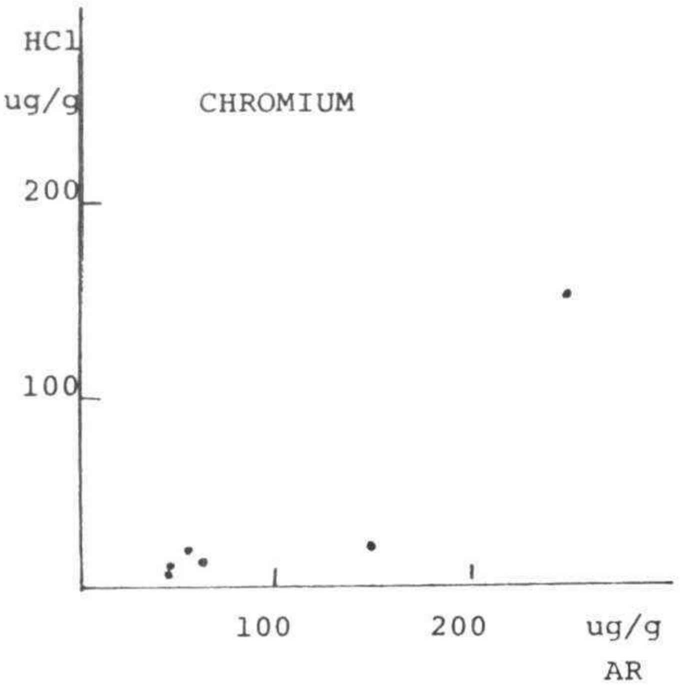
COLD HCl vs AQUA REGIA (1)

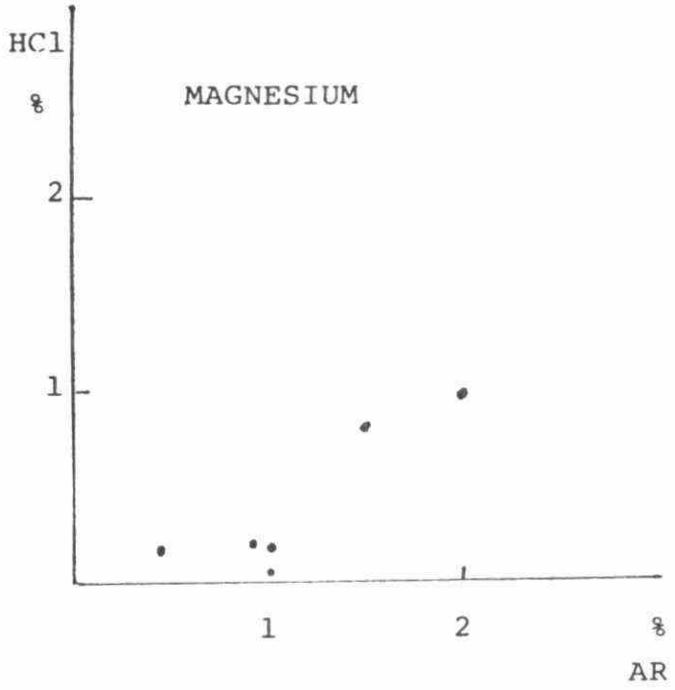


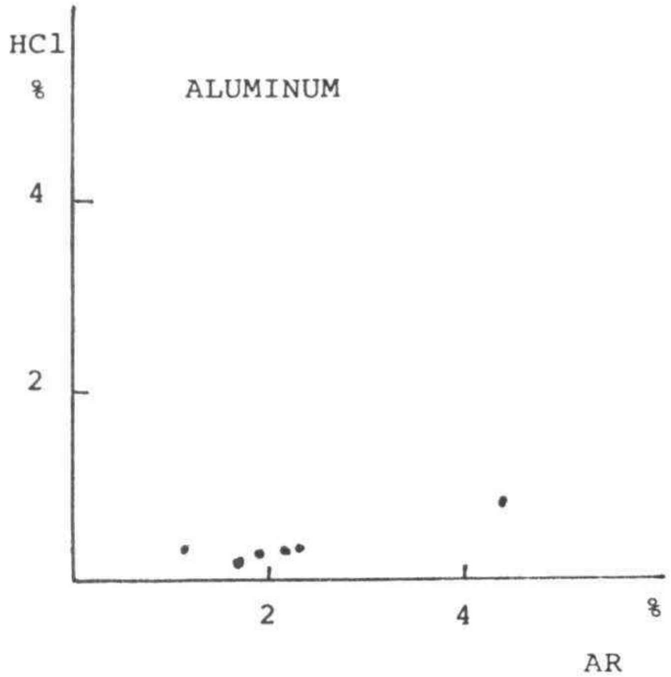
COLD HCl vs AQUA REGIA (2)

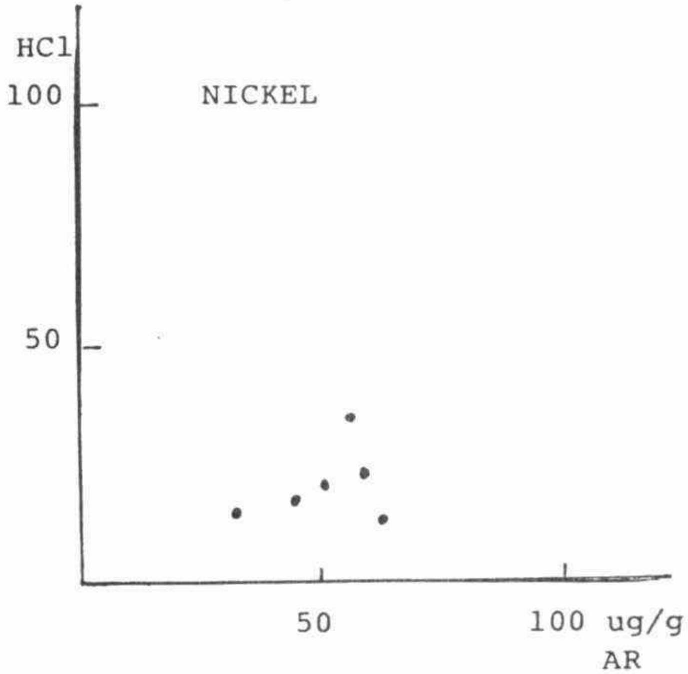


COLD HCl vs AQUA REGIA (3)







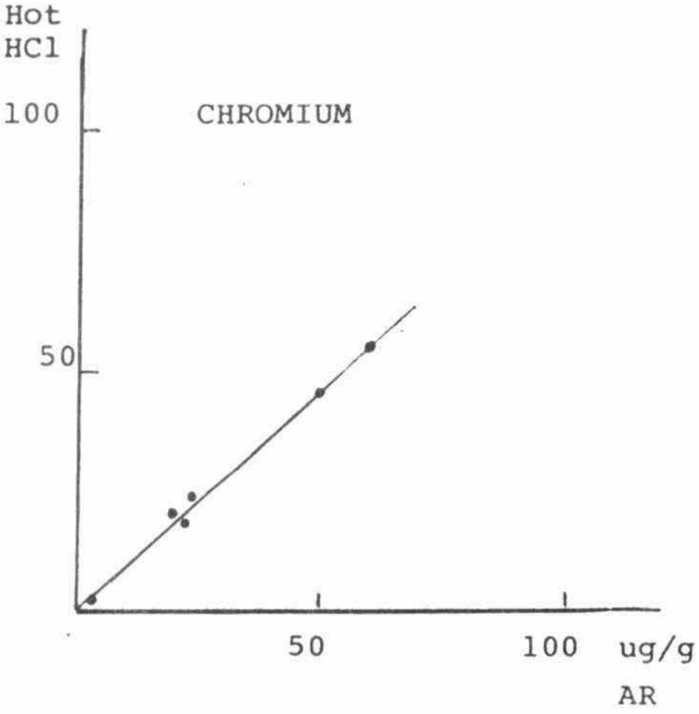


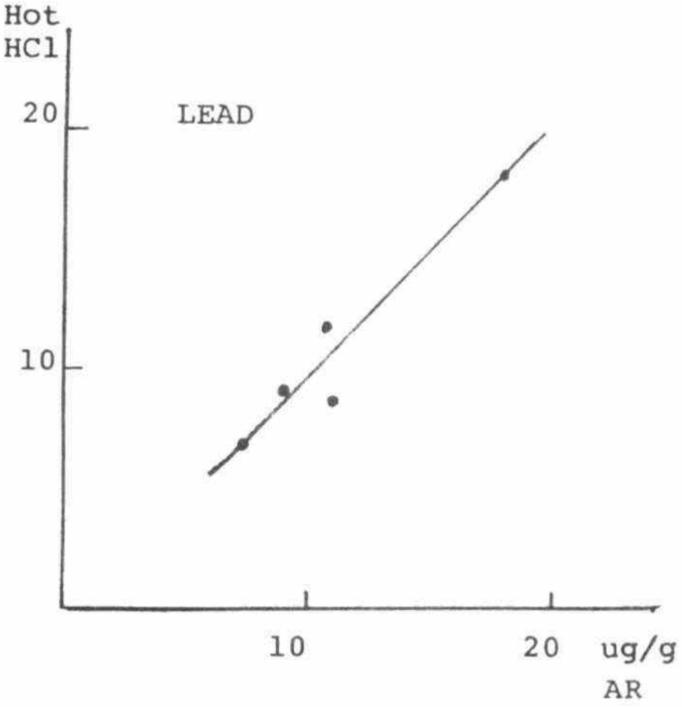
2) Hot dilute HCl Digestion

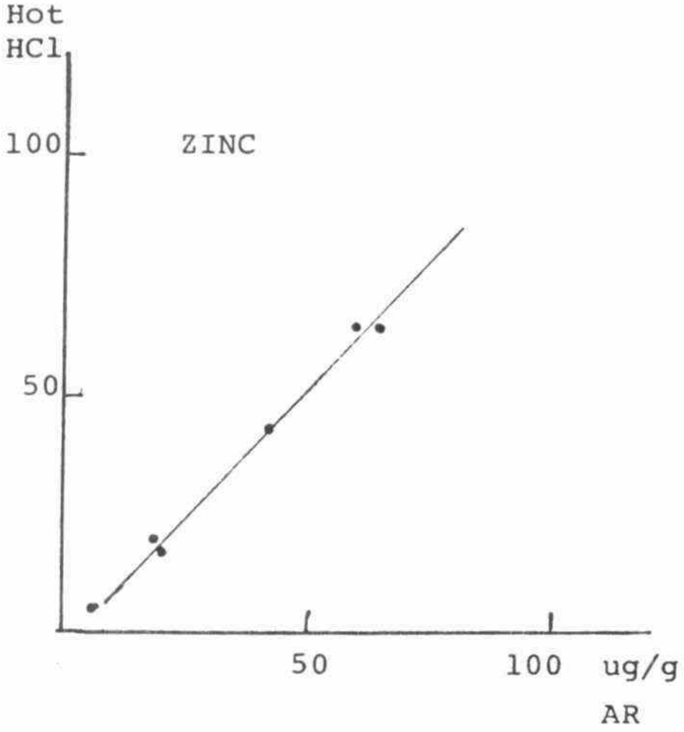
Six in-house reference samples of sediments and soils were analyzed by the McKown procedure and the results compared with mean values for routine HCl/HNO digestion (Koch 1977)*. Strong correlations were obtained for all metals tested except selenium. There was insufficient data for Co, Mo or V because of detection limit problems with the HCl/HNO_3 procedure. Concentrations were marginally higher by the HCl/HNO_3 procedure method for Cr, Al, Pb and Zn but larger differences were obtained for As, Mn, Cd, Cu and Ni.

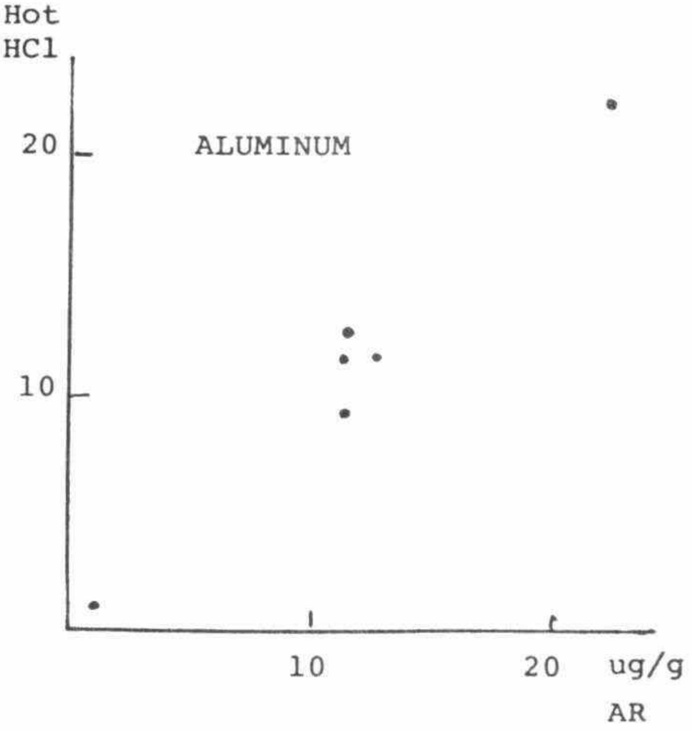
* KOCH, L., 1977. A Comparison of a Method Proposed by ASTM with a Method Standardly used by The Ontario Ministry of Environment to Test for 21 Extractable Metals in Sediments. University of Waterloo, Ontario Work Report. Unpublished.

HOT HCl vs AQUA REGIA (1)









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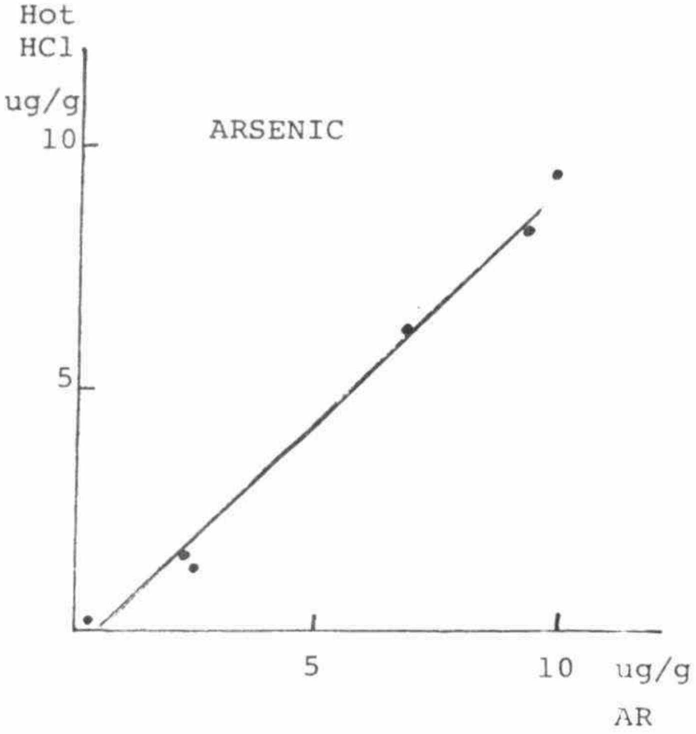

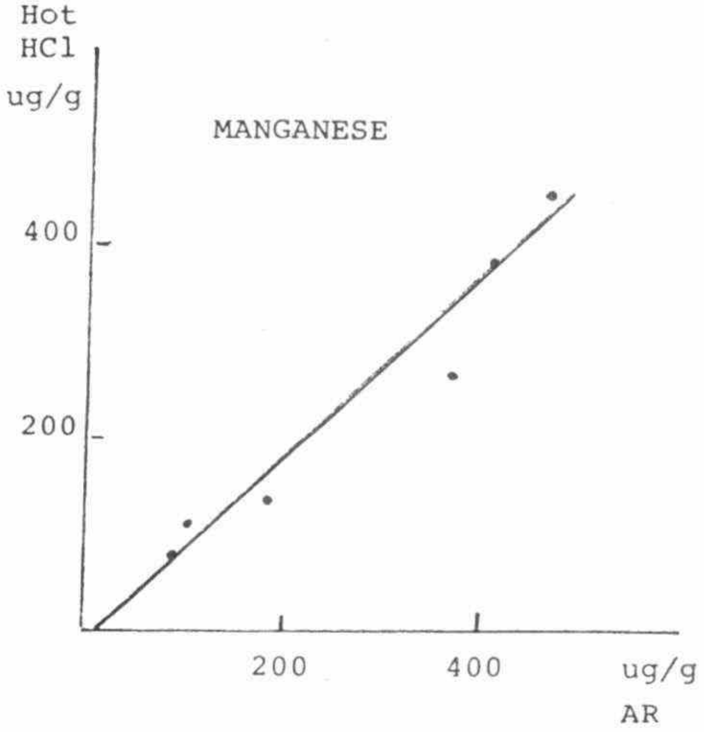

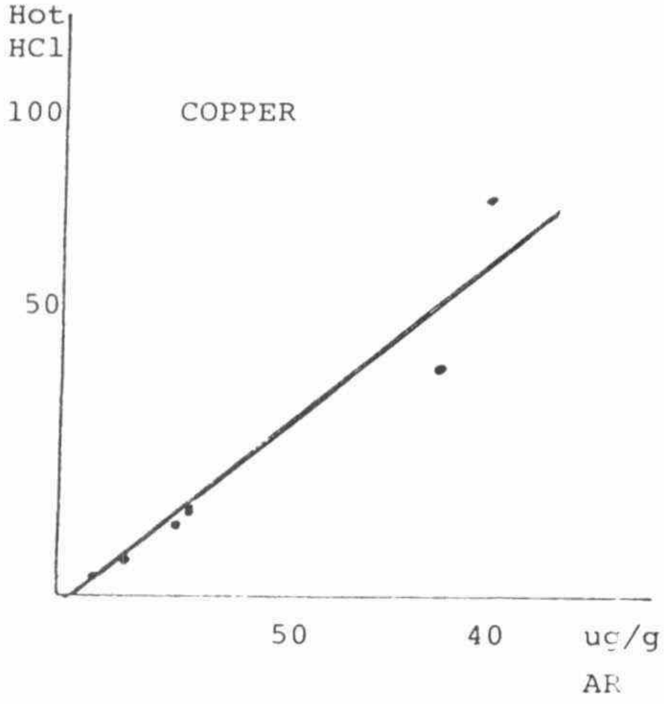

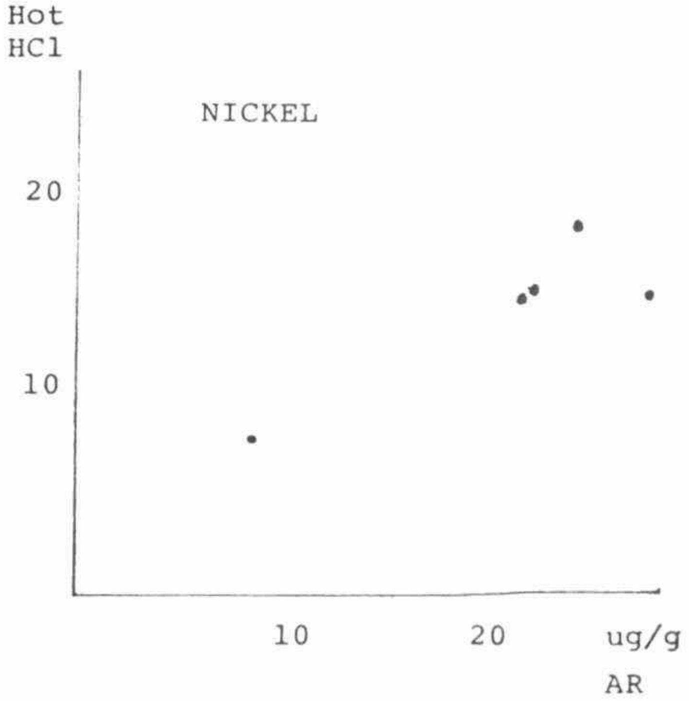

DISCUSSION

More extensive testing of both procedures is required before firm conclusions can be drawn of the relative merits of the three methods. Higher proportions of extractable metals can be expected for HCl/HNO3 digestion because of at least partial destruction of organic matter, the higher acid/sample ratio and, compared with the 0.5 N HCl method, the action of heat.

Of particular interest is the lack of a relationship between HCl/HNO3 and 0.5 N HCl for Cr, Mg, Al and Ni which would suggest that HCl/HNO3 is not measuring the environmentally significant fraction for these metals.

There are advantages and disadvantages to all three methods. HCl/HNO3 has the advantages of small sample size and removal of organic matter, facilitating analysis by atomic absorption spectrophotometry (AAS) or inductively coupled plasma (ICP). The 0.5 N HCl and hot dilute HCl methods have better detection limits than HCl/HNO3 because of lower dilutions (1:20, 1:6.25 and 1:50 or 100, respectively). On the other hand, the lower dilutions and presence of organic matter in the first two methods could lead to interferences in AAS analysis.

Similar studies are required for soils and sewage sludges. It is planned to evaluate the use of DTPA as an extractant in shake tests. Evaluation of various extractants, including DTPA and leaf extracts is also planned for column leach tests with industrial wastes and mine tailings.

CONCLUSIONS

Correlations can be obtained between heavy metal fractions extracted by the OMOE aqua regia ($HCl:HNO_3$) and hot dilute HCl digestion procedures. There is agreement for some metals but not for others with cold dilute HCl extraction. The digestion procedures may, therefore, be releasing larger proportions of some metals from the "residual" minerals of sediments, as indicated by the lack of correlation for Cr, Mg, Al and Ni.

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APPENDIX

ANALYTICAL PROCEDURES

OMOE AQUA REGIA DIGESTION

(1) One gram and one-half gram portions of each sample were placed in Phillips Beakers. Two blanks were also provided in each run.

(2) To the one gram sample beakers the following was added in succession:

(a) 10 ml concentrated nitric acid (reagent quality)

(b) 20 ml concentrated hydrochloric acid (reagent quality)

To the one-half gram sample beakers half the amount of each acid was added.

(3) The beakers were then placed on a hotplate which was set at 100°C.

(4) The beakers were removed when each sample had gone down to dryness. Then 5 ml of concentrated hydrochloric acid and 5-10 ml of distilled water was added to the residue in each beaker. The beakers were returned to the hotplate for an additional 15 minutes. After this time period the beakers were removed and allowed to cool to room temperature.

(5) The solutions were quantitatively transferred to volumetric test tubes. The volume within each test tube was brought up to 50 ml with distilled water.

DILUTE HCl EXTRACTION

1) Sieve air-dry sediment through 70 mesh* nylon screen
2) Weigh 5 g into plastic bottles (200 ml) and add 100 ml of 0.5 N HCl
3) Shake overnight (16 hr) on wrist-action shaker at high speed
4) Filter and submit for AAS analysis

* - 80 mesh fraction was used by Agemian & Chau, 1976. This mesh size was not available in nylon at the time of the test.

HOT DILUTE HCl DIGESTION

(1) Four grams of each sample were placed in 150 ml beakers. Duplicates of each sample were provided in each run. Two blanks were also provided to ensure that there was no contamination by the acids or water used during the run.

(2) To each beaker containing sample and to the blanks the following was added in succession:

(a) 100 ml distilled water

(b) 1 ml of concentrated nitric acid (reagent quality)

(c) 10 ml of concentrated hydrochloric acid (reagent quality)

(3) The beakers were then covered with ribbed watchglasses and placed on a hotplate set at 95°C.

(4) The beakers were removed from the hotplate when the volume of the remaining solution was between 10 and 15 ml. The beakers were then allowed to cool to room temperature.

(5) The solutions were then quantitatively filtered into volumetric test tubes. The volume within each test tube was then brought up to 25 ml with distilled water.